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Seasonal Variations in Organic Emissions for Significant Sources of Volatile Organic Compounds

Pacific Environmental Services, Inc, Santa Monica, CA

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SEASONAL VARIATIONS IN ORGANIC EMISSIONS FOR SIGNIFICANT SOURCES OF VOLATILE ORGANIC COMPOUNDS

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

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16. ABSTRACT

Discrepancies between rates of emission of VOC determined on an annual basis and those occurring in summer were studied, using as example areas Tampa Bay, St. Louis and Buffalo. Reactive VOC's were estimated by correcting total VOC's for methane content. A methodology for adapting VOC inventories to reflect summer emission patterns is outlined. The indicated increase in rate of emissions due to summer conditions ranged from 3 to 14 percent, as applied to the estimated annual non-methane emissions.

Corrections for methane and for summer conditions did not appreciably change the order of importance of emission source categories.

The effect of temperature is the principal cause of increased VOC emissions in summer. At least 80 percent of VOC's came from gasoline-powered vehicles and from evaporation of solvents and petroleum products. Vehicle exhaust emissions decrease as ambient temperature increases, but this effect is not large enough to counterbalance the enhanced gasoline losses from marketing and storage at summer temperatures. Improved controls on evaporative emissions could change the relative importance of exhaust and evaporative effects.

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EXECUTIVE SUMMARY

To investigate the magnitude of discrepancies between rates of emission of volatile organic compounds (VOC's) determined on an annual basis and those occurring during the summer season, PES studied the significance of sources during the summer season for three areas where oxidant air quality standards have been exceeded. Reactive VOC's were estimated by correcting total VOC's for methane content.

A methodology for adapting annual VOC inventories to reflect summer emission patterns is outlined.

Areas studied were Tampa Bay, Florida; St. Louis, Missouri; and Buffalo, New York. Basic data on emissions were provided by output from the National Emissions Data System (NEDS) file. For the Tampa Bay Area, more detailed data were available from a concurrent study directed toward the development of a detailed VOC inventory for use in a photochemical air quality simulation model.

Estimated total annual emissions were about 75,000 metric tons (MT) for Tampa Bay, 297,000 MT for St. Louis, and 120,000 MT for Buffalo. Estimated methane emissions ranged from 1 to 3 percent of the total. The indicated increase in rate of emissions due to summer conditions was from 3 to 14 percent, applied to the estimated annual non-methane emissions.

Corrections for methane and for summer conditions did not appreciably change the order of importance of emission source categories. In each area at least 80 percent of the organic emissions came from three categories: gasoline-powered vehicles, solvent evaporation losses, and petroleum product evaporation losses.

The results show that the effect of changes in temperature is the principal cause of increased VOC emissions in the summer.

Seasonal variations due to changes in temperature may be small, as in Tampa Bay, or very substantial, as in St. Louis. In Tampa Bay the seasonal temperature variation is relatively small, and decreases in exhaust emissions partly offset increases in evaporative emissions. In St. Louis the seasonal temperatures vary widely, causing the increase in evaporative emissions to predominate in the overall 14 percent summer increase. Humidity was not found to be a factor in determining VOC emissions, nor did sunshine appear to have any appreciable effect.

Future improved controls on evaporative emissions could change the relative importance of exhaust and evaporative effects and should tend to reduce the overall seasonal effect. Again, the seasonal activity factor, which also affects the summer-to-annual ratio, could be more important at other times and places than it appears to be in the selected study areas. We may conclude that the magnitude of seasonal variation of reactive organic emissions is quite locale-specific. It may be of importance most especially in places where seasonal variations in either temperature or activity are large.

1.0 INTRODUCTION

1.1 BACKGROUND

Emissions of organic compounds into the ambient atmosphere are subject to regulation, primarily because vapors of these compounds participate in chemical reactions. Chemical reactions cause contamination of the atmosphere with photochemical oxidants, often leading to unacceptable air quality in both urban and rural locations. The objective of regulating reactive organic emissions is to prevent the accumulation of photochemical oxidants to concentrations exceeding the National Ambient Air Quality Standards (NAAQS).

The highest observed concentrations of photochemical oxidants occur during the summer season due to meteorological conditions which are most conducive to oxidant formation in that season. To implement oxidant air quality control by reduction of organic emissions, therefore, it is necessary to promulgate control measures which relate especially to those emissions which occur in the summer months. Present organic emission inventories are usually compiled on an annual basis; thus they may not accurately reflect quantities of emissions which occur in the summer months.

To investigate the likely magnitude of discrepancies between emission rates determined on an annual basis and those occurring during the summer season, the Source Analysis Section, Air Management Technology Branch, Office of Air Quality Planning and Standards of the U.S. Environmental Protection Agency contracted with PES. Under EPA Contract No. 68-02-2583, Task Order No. 6, PES was directed to determine the significant souces of reactive organic emissions during the oxidant season, i.e., the quarter-year, July through September, for three geographic areas where violations of the air quality standard for oxidants have occured.

Because only the nonmethane fraction of total organic emissions is reactive and leads to the formation of oxidants, only variations in nonmethane organics are relevant to the issue of oxidant control. PES was therefore directed to determine nonmethane fractions of the significant emissions wherever possible, and to determine the difference in inventories corresponding to this correction.

Present EPA policy is that three other organic compounds (in addition to methane) are of negligible photochemical reactivity and should be exempt from regulation under State Implementation Plans. These compounds are ethane, 1,1,1-trichloroethane, and trichlorotrifluoroethane (Freon 113). Therefore, identifying the nonmethane hydrocarbons with the reactive organic compounds is not strictly correct. However, the latter two compounds constitute only a small fraction of the total solvents used and are not expected to have unusual seasonal distributions. At the same time, the principal sources of ethane are the same as the principal sources of methane, viz., exhaust gases from internal combustion engines and from combustion of natural gas. In such emissions, the ethane content is usually only 5 or 10 percent of the methane content. For the purpose of this report, therefore, emissions of these compounds are considered to be negligible.

The most significant sources of total organic emissions, on an annual basis, nationwide, were listed in the Task Assignment and are shown in Table 1-1. For each of these source categories, PES was directed to determine the effects of differences in ambient temperature and activity level between the summer months and the year as a whole, for each of the three chosen geographical areas. Any additional sources which might be locally significant were to be identified, and other factors such as sunlight and humidity were to be investigated.

Table 1-1. SIGNIFICANT SOURCES OF TOTAL ORGANIC EMISSIONS[a]

1.	Gasoline-powered vehicles
2.	Solvent evaporation loss
3.	Petroleum product storage and evaporation losses
4.	Petroleum refineries
5.	Open burning
6.	Chemical manufacturing
7.	Stationary fuel combustion
8.	Carbon black production
9.	Aircraft
10.	Diesel-powered vehicles

[a] Listed in order of importance on an annual, nationwide basis.

Finally, PES was directed to develop a preliminary outline of a methodology for adapting annual inventories of organic emissions to reflect the emission patterns of the summer quarter.

1.2 STUDY AREAS

After consultation with the project officer, it was decided that the geographical areas to be investigated would be:

- Tampa Bay, Florida: the air quality control region comprising Hillsborough County and Pinellas County. This is a southern area having mild winters and fairly high summer temperatures. (It was also subject of another PES study, "Assessment of the Anthropogenic Hydrocarbon and Nitrogen Oxide Emissions in the Tampa Bay Area," under EPA Contract No. 68-02-2606, Task Order No. 2).

- St. Louis, Missouri: the area comprising the City and County of St. Louis and six adjoining counties, namely, Madison, Monroe, St. Clair, Franklin, Jefferson, and St. Charles. This area is part of the St. Louis Interstate Air Quality Control Region. It is a midwestern location with relatively severe winters and hot summers, and is a major center of chemical industry.

- Buffalo, New York: the area comprising Erie County and Niagara County in "upstate" New York, having very severe winters but somewhat lower average summer temperature than the other areas chosen. Buffalo, the major city in the area, has a rather substantial chemical industry.

1.3 DATA SOURCES

Basic data on emissions were provided by output from the National Emissions Data System (NEDS) file. This information was furnished in the form of County Emissions Reports for each of the counties in the selected areas, except that the City of St. Louis was the subject of one such report while St. Louis County, excluding the city, accounted for another. Thus, there were eight such reports for the St. Louis area, two for the Tampa Bay area and two for the Buffalo area.

Information regarding the methane content of emissions from various source categories was taken from the PES draft report on emissons in the Tampa area, cited previously. Climatological information was obtained from the U.S. National Weather Service, or from the Climatic Atlas of the United States, reprinted by the National Oceanic and Atmospheric Administration in 1977 (Asheville, N.C.).

Information regarding the effect of temperature and other factors on emission rates was principally abstracted from "Compilation of Air Pollutant Emission Factors," Publication No. AP-42 of the USEPA. With specific reference to motor vehicle emission factors, latest information was obtained from "Mobile Source Emission Factors," an Interim Document of June 1977, prepared and distributed by EPA Office of Transportation and Land Use Policy (OTLUP). This document has since been published in a final version, EPA-400/9-78-005, March 1978.

Information regarding the seasonal variation of motor vehicle traffic and other activities causing organic emissions was obtained

from a wide variety of sources, especially from personnel of EPA Regions I, II, IV, and VII and of the states of Florida, Missouri, and New York, (Acknowledgements are provided in Section 6.0).

1.4 FINDINGS AND CONCLUSIONS

Table 1-2 summarizes the estimated emissions totals for the three study areas, as well as the corrections used to obtain the estimated nonmethane emissions and the summer emission rates. Estimated total annual emissions were about 75,000 metric tons (MT) for Tampa Bay,* while for St. Louis* they were 297,000 MT and for Buffalo* 120,000 MT. Estimated methane emissions amounted in each case to about 1 to 3 percent of the total. The indicated increase in rate of emissions due to summer conditions was from 2 to 14 percent, applied to the estimated annual nonmethane emissions.

Detailed results indicated that the corrections for methane emissions and for summer conditions of temperature and activity did not appreciably change the order of importance of the emission source categories from that found in the NEDS reports for annual emissions. In each area at least 80 percent of the organic emissions came from the first three categories (gasoline-powered vehicles, solvent evaporation losses, and petroleum product evaporation losses).

In Tampa Bay, organic emissions from vessels were estimated at about 5 percent of the total, making this the fourth most significant source category in that study area. Although vessels were also significant sources in St. Louis and Buffalo, their quantitative contribution was only one-half to one percent of total emissions in those areas.

Humidity was not found to be a factor in reactive organic emissions, nor was any evidence seen that sunshine causes significant increases in emissions from storage tanks or other sources.

* The terms "Tampa Bay," "St. Louis" and "Buffalo" hereinafter refer to the respective study areas, as described in Section 1.2.

Table 1-2. EMISSIONS ESTIMATES AND CORRECTION FACTORS

	Tampa Bay	St. Louis	Buffalo
Total annual organic emissions, 10^3 MT/yr	74.7	297	120
Methane emissions, as percent of total	3.1	1.4	2.4
Methane-free emissions, 10^3 MT/yr	72.4	293	117
Ratio of emission rates, summer/annual	1.03	1.14	1.08
Methane-free emissions, summer, 10^3 MT/yr	74.8	333	127

For example, emission factors for hydrocarbons from motor vehicles and from storage tanks, as presented in AP-42 ("Compilation of Air Pollutant Emission Factors"), are given by equations which depend on temperature and various other factors, but do not depend on humidity or solar radiation.

These results show that the effect of seasonal variations in organic emissions due to changes in temperature may be small, as in Tampa Bay, or very substantial, as in St. Louis. In Tampa Bay the seasonal temperature variation is relatively small, and decreases in exhaust emissions partially offset increases in evaporative emissions. In St. Louis the seasonal temperatures vary widely, causing the evaporative increases to predominate in the 14 percent summer increase. Future improved controls on evaporative emissions could change the relative importance of exhaust and evaporative effects. Again, the seasonal activity factor, which also affects

the summer-to-annual ratio, could be more important at other times and places than it appears to be in the selected study areas. PES therefore believes that it would not be wise to conclude, on the basis of these results, that the seasonal variation of reactive organic emissions is a reliably negligible effect.

1.5 ORGANIZATION OF REPORT

Calculations and other details supporting these findings are set forth in the ensuing sections of this report. Estimation of reactive organic emissions by correcting total organic emissions for methane content is discussed in Section 2.0. The seasonal variation of emissions from various source categories is reviewed in detail in Section 3.0. In Section 4.0, the methodology developed for correcting total annual emissions inventories to summer reactive emissions inventories is first outlined, then illustrated through application to three study areas.

Section 5.0 presents discussion of the results and conclusions derived therefrom, while Section 6.0 provides acknowledgments to those who helped by providing necessary information for this project.

2.0 ESTIMATION OF REACTIVE ORGANIC EMISSIONS

2.1 GENERAL

"Reactive organic emissions," for the purpose of this study, are defined as all volatile organic compounds except methane.* In order to estimate reactive organic emissions when total emissions of volatile organic compounds are known, the fraction constituted by methane is estimated and subtracted from the total.

In the following section, information about the methane fraction in emissions from various source categories is reviewed and factors for calculating reactive organic emissions (ROC) are developed.

2.2 METHANE CORRECTION FOR ORGANIC EMISSIONS

Methane is a common constituent of emissions from combustion of fuels, including exhaust gases from internal combustion engines. It is a principal constituent of natural gas and is, therefore, particularly abundant in flue gases from combustion of natural gas. It is not a constituent of organic solvents, nor does it occur in emissions caused by evaporation of solvents. Emissions caused by evaporation of hydrocarbons from crude oil may contain a small proportion of methane.

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*The nonmenclature of organic emissions in air pollution parlance has been rather confusing for some years, but recently changes have been proposed which may result in needed improvements. Known, loosely, as "hydrocarbons" (HC) from before the inception of the USEPA, they have more recently been referred to as "volatile organic compounds" (VOC). When a method was developed to determine methane concentrations separately, the difference between total VOCs and methane became known as "nonmethane hydrocarbons" (NMHC). Since methane is considered to be an unreactive organic compound (in the sense of promoting or not promoting the chemical reactions which occur in photochemical oxidant production), it is omitted from the "reactive organic emissions," which are therefore equivalent to the former NMHCs. Three other unreactive compounds of minor significance are discussed in Section 1-1.

The composition of organic emissions from the types of sources encountered in Tampa Bay was recently reviewed by PES as part of the study, "Assessment of Anthropogenic Hydrocarbon and Nitrogen Oxide Emissions in the Tampa Bay Area," EPA Contract No. 68-02-2606, Task Order No. 2. Table 2-1 presents the estimated methane content of emissions from the sources condidered in that study, except for vehicle exhaust emissions. The methane content for a 1976 U.S. mix of all gasoline vehicles was derived from the MOBILE-1 program (discussed below in Section 3.3.1). The program calculates total and nonmethane hydrocarbon emissions, combining both exhaust and evaporative into one figure. the evaporative emissions are also given separately by vehicle class. By subtracting the weighted sum of evaporative emissions, for all classes combined, from the total emissions, the exhaust emissions with and without methane were calculated. The difference (methane content) was 5.48 percent of the total, rounded off to 5 percent for Table 2-1. (The calculation was made for 75°F, since there was little variation with ambient temperature.)

Methane correction factors for the source categories used in this study, derived from the information in Table 2-1, are shown in Table 2-2. Reactive organic emissions are estimated by multiplying total organic emissions in any category by the appropriate correction factor.

Table 2-1. METHANE CONTENT OF ORGANIC EMISSIONS

Source of Emissions	Methane Content (C atom %)
Aircraft	
Jet exhaust, kerosene fuel	5
Piston engine exhaust	9
Stationary fuel combustion	
Coal	15
Fuel oil, distillate	11
Fuel oil, residual	11
Natural gas	20
Liquified petroleum gas (LPG)	10
Gasoline-powered vehicle exhaust	5
Diesel-powered vehicle exhaust (all)	2
Light-duty equipment (gasoline)	10
Rail Locomotives (diesel)	6
Small craft and boats (gasoline)	10
Ocean vessels (diesel fuel)	6
Ocean vessels (residual oil fuel)	11
Incineration of solid waste	34

Source: Table 2.2.5-2, "Assessment of the Anthropogenic Hydrocarbon and Nitrogen Oxide Emissions in the Tampa Bay Area," Draft Final Report, Pacific Environmental Servies, Inc.

Table 2-2. METHANE CORRECTION FACTORS BY SOURCE CATEGORY

	Source Category	Methane Correction Factor
1.	Gasoline-powered vehicles	
	Exhaust emissions	0.95
	Evaporative emissions	1.0
2.	Solvent evaporation	1.0
3.	Petroleum product evaporation	1.0
4.	Petroleum refineries	1.0
5.	Solid waste disposal	.66
6.	Manufacturing	1.0
7.	Stationary fuel combustion	.85
8.	Carbon black production	.62
9.	Aircraft	.93
10.	Diesel-powered vehicles	.98
11.	Vessels	.91

3.0 SEASONAL VARIATION OF EMISSIONS BY SOURCE CATEGORY

3.1 GENERAL

Seasonal variations in emissions are due primarily to two causes: seasonal changes in the rate of activities which yield emissions, and seasonal changes in temperature which cause differences in emission factors relating to organic emissions, independent of any changes in the basic activity rates.

3.2 ACTIVITY RATES

Considering first the effects of seasonal changes in activity rates, it is clear that such changes should cause directly proportional changes in emissions, so long as the operative emission factors do not change with changes in activity; this is certainly true for the great majority of souce types recognized as emitters, and it has been assumed true for all souces in this study.

Vehicle transportation is normally the largest source of organic emissions in urban areas. Seasonal variations can be estimated either by traffic surveys or by monitoring the rates of fuel usage for vehicle transportation. Traffic surveys commonly show combined results for all vehicles used on streets and highways and do not discriminate between gasoline- and diesel-powered vehicles. However, the proportion of diesel-powered vehicles in the urban vehicle population is normally small enough so that no substantial error will be caused if the combined variations are taken to apply to gasoline-powered vehicles and diesel vehicles severally. Off-highway vehicle use is not reflected in traffic surveys.

The variation of gasoline consumption with season provides an alternative index to rates of vehicle use. This index reflects off-highway use of gasoline-powered vehicles, but does not include diesel-powered vehicles either on or off streets and highways.

Vehicle activity factors* for Tampa Bay were, in this study, derived from traffic count information compiled monthly for several years for 12 survey stations (these data had been supplied previously for the PES gridded emissions inventory project, mentioned in Section 1.2). For St. Louis, monthly gasoline sales registered by the State of Missouri were used. For Buffalo, the State of New York provided gasoline consumption data for each of the two counties involved (Erie and Niagara).

Activity factors for petroleum product evaporation were assumed to be the same as those for vehicle transportation. This assumption seems eminently appropriate for the emissions due to service station operations. While it may be more questionable for the activity of storage and transportation of petroleum products, this source appears to be relatively minor.

A substantial fraction of emitted organics is attributed to solvent evaporation from area sources in the standard NEDS inventory. Methodology for estimating this contribution is to assume a per capita emission rate, currently 24 pounds per year; this is the amount required to account for the difference, nationally, between amounts of solvent manufactured and amounts accounted for in known industrial and commercial uses.

It is quite possible that the activity rates involved in various solvent-using processes may have appreciable seasonal components. Unfortunately, no specific information to this effect has come to light, so there is at present no basis for estimating a

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* For this study, the activity factor is defined as the ratio of the average monthly activity rate for the 3-month period, July through September, to the average monthly activity rate for an entire year. An activity factor of 1.0 represents no change in production in summer.

summer activity factor for this source. Structural painting is probably a somewhat seasonal activity, especially in the harsher northern climate of Buffalo. However, the amount of solvent used in this application appears to be only about one tenth of the total solvent attributed to area sources. Lacking more specific information, an activity factor of 1.0 has been assigned to this source.

Of the remaining source categories, only the emissions from industry are of sufficient magnitude to require specific attention as regards activity factors. Only in the St. Louis area did the total organic emissions from all industry exceed 10 percent of the total inventory. The only obvious basis for determining an industrial activity factor would be a seasonal index of either industrial production or industrial employment. Modification to such an overall industrial activity factor might be needed if a particular industry with a well-defined annual cycle of operations happened to account for a large fraction of industrial organic emissions in a study area. However, this circumstance has not been encountered in the present study.

To investigate this point further, PES obtained NEDS point source emission reports for Erie County, where the City of Buffalo is located. These reports identified 21 industrial plants emitting a total of 3,000 English tons of hydrocarbons per year. Of 66 point sources at the 21 plants, only one was reported to show any seasonal variation at all; in that case, with total annual emissions of 12 tons (11 metric tons), summer emissions were reported to be 26 percent of the annual; this corresponds to an activity factor of 1.04. These results suggest that seasonal variation in emissions in industries emitting major amounts of organics is likely to be very minor; accordingly, an activity factor of 1.0 has been assigned to these categories.

The remaining source categories -- solid waste, stationary fuel combustion, carbon black manufacture, aircraft, diesel vehicles, and vessels -- together contributed less than 10 percent of the estimated emissions in each study area. Since there is no obvious reason to expect extreme seasonal fluctuations in these activities, and since moderate variations would have only very minor effects on the overall inventory, activity factors of 1.0 have been assigned to these categories also.

3.3 EFFECTS OF TEMPERATURE

Emission rates for organics from various source categories have different sensitivities to changes in temperature. Of the major categories listed in Table 1-1, it is reasonable to expect gasoline-powered vehicles and petroleum product evaporation to be most affected by summer temperatures. Solvent evaporation losses are likely to be less affected because in many applications all solvent used in evaporated, so that the quantity entering the atmosphere is determined by the particular operation, independent of temperature.

The following sections discuss the principles applied in estimating temperature correction factors for emissions from various source categories.

3.3.1 GASOLINE-POWERED VEHICLES

Contaminants are emitted into the atmosphere from gasoline-powered vehicles in three principal modes:

- In exhaust gases
- In vapors lost from the fuel tank and carburetor due to heating and agitation
- In gases forced out of the motor through the crankcase

Organics in the exhaust of vehicles in transit are sensitive to temperature because such emissions are minimal after the engine has achieved a steady operating temperature; when the vehicle is at a low temperature when started, as in winter, the engine takes longer to reach its steady operating temperature (that is, to "warm up") than when the vehicle is warmer on starting. Accordingly, an increase in ambient temperature leads to reduced emissions of organics from this mode of operation.

The use of an air conditioner on a vehicle has the opposite effect, since with it the engine is more heavily loaded and consumes more fuel. The increased use of air conditioners at higher ambient temperatures increases exhaust hydrocarbon emissions. The theoretical maximum hydrocarbon increase (between absence of air conditioner usage and presence of operating air conditioners on all vehicles) is 13 percent. (For CO and NO_x emissions, this increase could theoretically reach a maximum of 18 percent. These figures are based on factors given in "Mobile Source Emission Factors," March 1978).*

Emissions from the crankcase of vehicles in transit are not known to be sensitive to temperature. According to OTLUP, emissions from this source are much less important, quantitatively, than they were 10 years ago, because more recent vehicle models have generally incorporated crankcase ventilation systems. For this reason, recently published emission factors combine crankcase emissions with evaporative emissions.

Emissions caused by evaporation of fuel carried in the vehicle are sensitive to temperature, because the volatility of the fuel is sensitive to temperature. Volatility is directly related to the

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* Mobile Source Emission Factors, EPA-400/9-78-005, March 1978

true vapor pressure of the gasoline, which increases by a factor of about 1.2 for each 10°F of increased temperature.

A computer program "MOBILE-1", supplied on tape by EPA to PES, was used to develop the temperature/exhaust hydrocarbon emission relationship. There are numerous input variations to this program to permit its use in different situations. For our purposes most input factors used were "default" options, based either on average national data or on the conditions used in the Federal Test Procedure for vehicle exhaust emissions. The route speed and average speed in all three test modes was arbitrarily set at 30 miles per hour. It was assumed that there was no air conditioner usage (for reasons discussed later), no extra vehicle loading, and no trailer towing. The proportions of vehicle miles accumulated in various test modes were taken from the earlier Tampa Bay study cited previously.

The program was run for a series of ambient temperatures with vehicle and mileage distributions for the calendar year 1976. The national average weighted distribution of vehicle types available in the program was used to develop the total emission factors for total and nonmethane hydrocarbons for all gasoline vehicle types combined. (This also includes about 3 percent diesel vehicles, which has no importance in developing the temperature correction factors.) Evaporative emissions were not included in these totals, which are reported in Table 3-1.

The ratios of summer to annual emissions can be derived from this table by the use of the two corresponding average temperatures. Thus the summer adjustment factor $F_e(t_s,t_a)$ is defined as:

$$F_e(t_s,t_a) = f(t_s)/f(t_a)$$

Table 3-1. EXHAUST HYDROCARBON EMISSIONS AT VARIOUS AMBIENT TEMPERATURES

Calculated by MOBILE-1 Computer Program for a Weighted Combination of All Vehicle Types

Ambient °F	Hydrocarbons (g/mi)	Nonmethane Hydrocarbons (g/mi)
0	6.67	6.28
5	6.43	6.06
10	6.22	5.86
15	6.02	5.67
20	5.83	5.50
25	5.67	5.34
30	5.51	5.20
35	5.37	5.07
40	5.23	4.94
45	5.11	4.83
50	5.00	4.72
55	4.90	4.63
60	4.80	4.54
65	4.71	4.46
70	4.63	4.38
75	4.56	4.31
80	4.49	4.25
85	4.42	4.19
90	4.37	4.13
95	4.31	4.08
100	4.26	4.03
105	4.21	3.99
110	4.17	3.95

where t_s is the average summer daytime temperature, t_a is the average annual daytime temperature, and $f(t_s)$ and $f(t_a)$ are computer-derived exhaust nonmethane hydrocarbon factors interpolated from Table 3-1.

The air conditioner usage factor deserves further comment. There were no data available to us on the fraction of vehicles equipped with air conditioners in the three study areas, nor on their degree of usage, either annually or in summer. Therefore no factor has been included for this effect. We suspect that the effect may not be negligible, in many cases. Using national average data on fraction of equipped vehicles and some plausible guesses about degree of usage based on average temperatures, we can roughly approximate what seasonal effects might be. The summer adjustment factor would be close to unity for Tampa Bay, where temperatures vary little with season. In St. Louis, on the other hand, where seasons are more extreme and summers are hot, the factor could be well above unity; we estimate it as roughly 1.07. Buffalo, which also has seasonal extremes, but cooler summers, might have a factor of about 1.05. These estimates are not based firmly enough for actual use, but they suggest the desirability of obtaining air conditioner usage data whenever possible for inclusion in these calculations.

The MOBILE-1 program will also calculate a single emission factor for crankcase and evaporative emissions. This apparently takes no account of the influence of ambient temperature. For the purposes of this study, therefore, a different method was used.

As a first approximation, the emission factor for organics from crankcase and evaporative emissions can be taken to be an exponential function of ambient temperature, proportional to the gasoline volatility function. This leads to a factor of about 2 percent increase for each degree (Farenheit) of increasing

temperature. Thus, the summer adjustment factor for crankcase and evaporative emissions can be approximated as $F_c(t_s,t_a)$, defined by

$$F_c(t_s,t_a) = \exp [0.02(t_s - t_a)] \qquad (1)$$

where t_s is the average summer daytime temperature, t_a is the average annual daytime temperature.

The temperature dependence of the net organic emissions from light-duty vehicles is, of course, the resultant of the effects of exhaust and of crankcase and evaporative emissions, weighted in terms of their relative importance. The factor F_e is less than unity when air conditioner usage is not considered. If air conditioner usage were allowed for, F_e would increase (but probably not above unity even in extreme cases). The factor F_c is greater than unity. The two opposing factors tend to diminish the sensitivity of the net emissions to changes in ambient temperature. This is shown in the example calculations for the three study areas, Sections 4.1 to 4.3

3.3.2 SOLVENT EVAPORATION LOSS

There seems to be no reason to believe that solvent evaporation losses, generally, are sensitive to changes in ambient temperature. Solvents are most commonly used in drycleaning and degreasing and as vehicles in inks, paints, and other surface coating materials. In these applications the amount of organic material which vaporizes is characteristic of the operation.

We therefore assume a temperature adjustment factor of 1.0 for emissions in this category.

3.3.3 PETROLEUM PRODUCT STORAGE AND EVAPORATION LOSSES

This source category is reported under two headings in NEDS County Emission Reports, namely, "Petroleum Storage and Transport"

for industrial point sources and "Gasoline Station Evaporation Loss" for miscellaneous area sources.

Petroleum storage and transport losses are reviewed in Section 4.3 of "Compilation of Air Pollutant Emission Factors." Various types of sources of organic emissions and their dependence on temperature, vapor pressure, and wind speed, as discussed in that document, are listed here in Table 3-2.

In these expressions, ambient temperature does not enter explicitly, but its variations exert their effects via the dependence of vapor pressure on temperature. As noted in Section 3.3.1, this effect amounts to 2 percent per degree Fahrenheit, which can be applied directly to those terms which are proportional to vapor pressure. On the other hand, the terms in P/(14.7-P) have a different temperature relation, which depends on the magnitude of the vapor pressure. For instance, if the vapor pressure is 11.8 psia, the denominator (14.7-P) is four times as sensitive to temperature as is the vapor pressure it self, and the sensitivity of the entire term, $[P/14.7-P)]^{0.7}$, is about 7 percent per degree; while, if P is 7.4 psia, the sensitivity is only about 3 percent per degree.

We must note, however, that these sensitivities are computed in terms of the temperature of the bulk liquid in the storage tank. Sensitivity to ambient air temperature will presumably be somewhat smaller than this, in most cases, because the tank contents do not rapidly reach ambient air temperature.

Another factor which tends to reduce the estimate of summer emissions is the customary practice of gasoline suppliers to market less volatile gasoline in the hot season, in order to help prevent problems with vehicle operation which are sometimes caused by excessive volatility of the fuel.

Table 3-2. EFFECTS OF TEMPERATURE AND OTHER FACTORS ON EMISSIONS OF ORGANICS IN PETROLEUM STORAGE AND TRANSPORT

Emission Source	Symbol	Variation Terms
Breathing loss (fixed-roof tanks)	L_B	$[P/(14.7-P)]^{0.68} (T)^{0.50}$
Working loss (fixed-roof tanks)	L_W	P
Standing Loss (floating-roof tanks)	L_S	$[P/(14.7-P)]^{0.7} V_W^{0.7}$
Withdrawal loss (floating-roof tanks)	L_{WD}	None
Filling loss (variable Vapor space systems)	L_V	P

P = true vapor pressure, psia

T = average ambient temperature change from day to night, °F

V_W = average wind velocity, miles per hour

Source: Compilation of Air Pollutant Emission Factors, AP-42, Section 4.3

In view of the imponderables involved in this estimate, it seems prudent to assume that the petroleum storage and transport emissions remain roughly proportional to gasoline vapor pressures and therefore increase with temperature at about 2 percent per degree Fahrenheit.

Standing losses from floating roof tanks are also sensitive to average wind velocity, increasing as wind velocity increases. Since wind velocities in summer are likely to be relatively low, particularly on days with weather conducive to oxidant formation, it is likely that this effect corresponds to a slight decrease in average emissions during the summer. Since it affects only one of a number of comparable terms in regard to storage emissions, we assume it can safely be neglected in calculating the temperature effect.

In regard to emissions from gasoline station evaporation losses, the following equation is cited in "Compilation of Air Pollutant Emission Factors," Section 4.4 (before Supplement 7, since the latter provides no indication of relationship to temperature):

$$L_D = 2.22\exp(-0.02645 + 0.01155T_{DF} - 0.01226T_v + 0.00246T_vP_{RVP}) \quad (9)$$

where

L_D = vapor displacement loss, $lb/10^3$ gal

T_{DF} = average dispensed fuel temperature, °F

T_v = average temperature of vehicle tank vapor displaced, °F

P_{RVP} = Reid vapor pressure of gasoline pumped, taken at storage temperature; psia

If the average Reid vapor pressure of gasoline were 10 psia and the dispensed fuel were at ambient temperature, the implied sensitivity of this emission source to ambient temperature would be about 2.4

percent per degree. However, since most service stations keep gasoline in underground storage tanks where it is fairly well insulated from the ambient air, the temperature sensitivity of emissions from such stations could be as little as 1.2 percent per degree. Since spillage constitutes a separate source of emissions from gasoline service stations and is not sensitive to temperature, we adopt the lower estimate (1.2 percent per degree) as applying to gasoline station evaporation losses.

3.3.4 PETROLEUM REFINERIES

We have no direct information as to the variation of petroleum refinery emissions with temperature. Process emissions are likely to be relatively constant throughout the year, depending mainly on the throughput rate. Fugitive losses, however, seem likely to increase in hot weather as pipes and exposed storage tanks and drums are heated by the sun. We assume a temperature sensitivity of 0.5 percent per degree Fahrenheit.

3.3.5 CHEMICAL MANUFACTURING

We assume that most of the organic emissions from chemical manufacturing are either process emissions or solvent evaporation losses, both of which are basically independent of temperature. We, therefore, assume zero temperature sensitivity, corresponding to a temperature adjustment factor of 1.0 for these emissions.

3.3.6 REMAINING SOURCES

Solid waste and incineration, stationary fuel combustion, carbon black manufacturing, aircraft, diesel-powered vehicles, and vessels all contribute relatively minor amounts of emissions to the urban total. There is no obvious reason why any of them should be

markedly sensitive to changes in temperature. We, therefore, assume a temperature adjustment factor of 1.0 for each of these categories.

3.3.7 SUMMARY OF TEMPERATURE CORRECTION FACTORS

The results of the computations discussed in Section 2.3 are summarized in Table 3-3.

Table 3-3. TEMPERATURE CORRECTION FACTORS FOR ORGANIC EMISSIONS

Source Category	Sensitivity, % per °F	Correction Factor for 10° Increase
1. Gasoline-powered vehicles		
Exhaust emissions	See note a	
Crankcase and evaporative	+2.0	1.22
2. Solvent evaporation losses	0.	1.00
3. Petroleum product losses		
Storage and transport	+2.0	1.22
Gasoline station evaporation	+1.2	1.13
4. Petroleum refineries	+ .5	1.05
5. Solid waste disposal	0.	1.00
6. Chemical manufacturing	0.	1.00
7. Stationary fuel combustion	0.	1.00
8. Carbon black production	0.	1.00
9. Aircraft	0.	1.00
10. Diesel-powered vehicles	0.	1.00
11. Vessels	0.	1.00

[a] Exhaust emissions are to be corrected by direct application of methodology explained in Section 3.3.1, using Table 3-1.

4.0 AREA STUDY RESULTS

4.1 OUTLINE OR PROCEDURE

The PES approach to estimating ROC emissions consists, basically, of the following steps:

1. Retrieve County Emission Summaries for all counties in the study area from NEDS, and tabulate HC emissions given therein for each of the source categories listed in Table 1-1 and for any additional categories which appear to be quantitatively important (contributing, for example, more than 1 percent of total emissions). Convert the figures to metric tons per year (MT/yr) if desired.

2. Estimate what fraction of the ROC emissions from gasoline-powered vehicles is attributable to exhaust emissions and what fraction to evaporative emissions. This proportion will vary, depending on the year of reference in the study. Emissions data retrieved for this study were assumed to represent 1976, and the fraction attributable to exhaust was estimated at 0.65. (See Section 4.2.2)

3. Ascertain emissions for petroleum storage and transport and for gasoline station evaporative losses, as separate parts of source category 3 (petroleum product storage and evaporation losses).

4. For each source category or subcategory, estimate correction factors for methane exclusion, for seasonal (summer) activity, and for temperature adjustment. (Where no correction is needed or none is available, the correction factor is 1.0, not zero).

   a. For methane exclusion, determine or estimate the typical methane content of the emissions in terms of weight percent or in terms of carbon atoms percent (not as mole percent or vapor volume percent). The correction factor is (100 - percent methane)/100.

   b. For seasonal activity, estimate average monthly activity rate during summer and during the year and take the quotient. For vehicle categories, the activity rate index may be vehicle-miles as indicated by traffic surveys or fuel consumption statistics for

the study area. For industrial categories, specific industry production or employment figures may be used, or more general statistics as to industrial employment in the study area. For emissions at gasoline stations, the same factor used for vehicle categories is appropriate. For the remaining categories, unless one of them proves to be an unusually large source, activity factors may be neglected.

c. For temperature adjustment, estimate the sensitivity (S_t) of emissions in each category to changes in temperature and determine, from local or national weather records, the average daily maximum temperature in summer (t_s) and year-round (t_a). The temperature adjustment factor is $\exp[S_t(t_s-t_a)/100]$. (S_t), given as percent per degree, is negative if emissions decrease when temperature increases. (For exhaust emissions from gasoline-powered vehicles, the temperature adjustment may be estimated from tables of emission factors or correction factors given as a function of temperature, as in Table 3-1. Evaporative emissions from vehicles, however, are treated in the same manner as other source categories).

5. Multiply the NEDS HC emissions for each category by all three of the correction factors appropriate to that category, obtaining a relative rate of emissions of reactive organics for the summer period, in units of tons or metric tons per year. Sum the relative rates for all categories to obtain a relative total rate of organic emissions for the study area, again in tons or metric tons per year. This is the desired result.

The following sections illustrate this procedure as applied to the three study areas selected for this project.

4.2 TAMPA BAY STUDY AREA

4.2.1 TOTAL ORGANIC EMISSIONS

Emissions data for Tampa Bay were obtained from two sources, the standard NEDS County Emissions Reports and, in addition, the draft report, "Assessment of the Anthropogenic Hydrocarbon and

Nitrogen Oxide Emissions in the Tampa Bay Area," prepared by PES under EPA Contract No. 68-02-2606, Task Order No. 2, March 1978.

Table 4-1 shows organic emission rates for each source category extracted from the NEDS reports for the two counties. In these NEDS inventories, motor vehicle emissions estimates were obtained using emission factors from Supplement 5 of AP-42 (prior to changes introduced in Supplement 8). Also shown are the totals for each county of all emissions in the categories listed, the total for each county as given in the NEDS report, and (by difference) the amounts of emissions in categories not included in the list. Other columns show the total area emissions in each category in short tons per year and metric tons per year, and the percentage (by weight) of total emissions contributed by each source category.

The PES survey of hydrocarbon emissions in the Tampa Bay Area gave results differing from the NEDS data in two ways. The major difference resulted from the use of MOBILE-1 to calculate the emissions from highway vehicles, which decreased the amount from gasoline vehicles by 6,700 MT per year. Various other emissions that had not been entered in the NEDS data base partially offset this, so that the total increased from 71,400 to 74,700 MT per year. Details of the revisions indicated by the PES survey are given in Table 4-2. The storage-and-transport subcategory was increased from zero to 6,100 MT/yr by emissions calculated for storage tanks, and industrial point sources of solvent evaporation, entered as manufacturing rather than chemical manufacturing, came to 2,700 MT/yr instead of zero. Aircraft emissions were estimated lower than in the NEDS report, but emissions from vessels more than made up the difference. Other categories increased were solid waste disposal and stationary fuel combustion, which includes fuel used in electric generating plants.

Table 4-1. TOTAL ORGANIC EMISSIONS, TAMPA BAY STUDY AREA

Source Category	Emission Rates		Total		Percent of Total
	Hillsborough tons/yr	Pinellas tons/yr	tons/yr	MT/yr	
1. Gasoline vehicles	29,500	24,900	54,400	49,500	69
2. Solvent evaporation	4,500	5,200	9,700	8,800	12
3. Petroleum product evaporation					
a. Storage transport	0	0	0	0	
b. Gasoline stations	3,100	3,300	6,400	5,800	8
4. Petroleum refineries	0	0	0	0	
5. Solid waste disposal	400		400	400	
6. Manufacturing	0	0	0	0	
7. Stationary fuel combustion[a]	100	300	400	400	1
8. Carbon black production	0	0	0	0	
9. Aircraft	2,400	300	2,700	2,400	3
10. Diesel vehicles	800	900	1,700	1,500	2
11. Vessels	1,100	300	1,400	1,300	2
Total, this list	41,900	35,200	77,100	70,100	98
Total, NEDS	42,800	35,700	78,500	71,400	100
Remainder unlisted	900	500	1,400	1,300	2

[a] This includes fuel burned in generating electricity.

Table 4-2. REVISED ORGANIC EMISSIONS, TAMPA BAY AREA

Source Category	NEDS Estimate MT/yr	PES Estimate MT/yr	Percent of Total
1. Gasoline vehicles	49,500	42,800	57
2. Solvent evaporation	8,800	8,800	12
3. Petroleum product evaporation			
a. Storage and transport	0	6,100	8
b. Gasoline stations	6,800	5,400	7
4. Petroleum refineries	0	0	
5. Solid waste disposal	400	800	1
6. Manufacturing[a]	0	2,700	4
7. Stationary fuel combustion	400	800	1
8. Carbon black production	0	0	
9. Aircraft	2,400	900	1
10. Diesel fuel vehicles	1,500	1,500	2
11. Vessels	1,300	3,300	4
Remainder unlisted	1,300	1,600	2
Total	71,400	74,700	

[a] This category has been broadened to include all recognizable industrial solvent use emissions.

4.2.2 PARTITION OF GASOLINE-POWERED VEHICLE EMISSIONS

The MOBILE-1 computer program calculations described in Section 3.3.1 were also used to determine the proportions of exhaust and evaporative gasoline vehicle emissions, since those used to generate the NEDS estimates were not known. In Table 3-1 the exhaust reactive organic emissions are listed for various temperatures. The evaporative emissions calculated in the same program were invariant with temperature. The same vehicle type mixture used for exhaust emissions was used to calculate the overall combined evaporative emissions, 2.20 g/mi. The ratio of exhaust to evaporative emissions then varies from 74/26 at 0°F to 64/36 at 110°F. Most of the change occurs in the lower part of the temperature range, however. In the temperature ranges used in this study a value of about 65/35 is suitable.

When these factors are applied to the total of 42,800 MT of organic emissions from gasoline-powered vehicles, subcategory totals are calculated to be 27,900 MT attributable to exhaust emissions, 14,900 to evaporation. (These numbers are carried to new lines as separte subcategories under category 1, gasoline-powered vehicles).

4.2.3 PETROLEUM PRODUCT EVAPORATION LOSSES

The NEDS listing for the study area indicated no emissions attributable to evaporation from storage tanks and trucks used with gasoline and other petroleum products. The PES survey, however, did identify a substantial number of storage tanks and provided an estimate of 900 MT of organic emissions annually from this subcategory.

A re-estimate of gasoline station evaporation losses by PES yielded a reduction of 400 MT/yr in these emissions, as indicated in Table 4-2.

4.2.4 CORRECTION FACTORS

4.2.4.1 Factors for Exclusion of Methane

The determination of reactive organic emissions requires information on the methane content of the total organic emissions (cf. Section 2.1). In the absence of specific information about the composition of emissions in the study area, methane fractions as determined in other studies for comparable emissions are used, taken from Table 2-1.

4.2.4.2 Summer Activity Factors

4.2.4.2.1 Vehicle Activity Factors

The seasonal aspect of vehicle activity in the Tampa Bay area was investigated through review of traffic information, furnished to PES originally by the Florida Department of Transportation for use in the emissions survey project previously cited. Vehicle counts were taken routinely at 12 selected stations representing area traffic and were compiled monthly over a period of several years. Using total monthly count as an index of vehicle activity, we estimate the factor to be approximately 0.98. This factor is applied to both subcategories of source category 1, (gasoline-powered vehicles), and also to subcategory 3b (gasoline station evaporation losses) and category 10 (diesel-powered vehicles).

4.2.4.2.2 Industrial Activity Factors

As explained in Section 3.2, most industrial sources of organic emissions seem to have no marked seasonal variations in activity. Since the PES survey provided no indications of such variations occurring in the study area, an activity factor of 1.0 has been assigned for the industrial emissions category.

4.2.4.2.3 Other Activity Factors

In the absence of any indications of marked seasonal variation, remaining activity factors have been assigned a value of 1.0.

4.2.4.3 Temperature Adjustment Factors

The temperature differential between summer and winter in Florida is rather small in comparison with many other parts of the United States, particularly inland areas such as St. Louis and Buffalo. Climatological data for the Tampa Bay area show that the average daily maximum temperature for the summer quarter, t_s, is 90°F while the average for the entire year, t_a, is 82°F. The differential, $t_s - t_a$, is only 8°F.

4.2.4.3.1 Exhaust Emissions

By the procedure described in Section 3.3.1 and values interpolated from Table 3-1, we find the correction factor for 82°F to 90°F for exhaust emissions to be 0.98.

4.2.4.3.2 Vehicle Evaporative Emissions

From Section 3.3.1, we apply Equation 1, which predicts the temperature adjustment factor as

$$F_c(80,72) = \exp(0.02 \times 8), \text{ or } 1.16.$$

4.2.4.3.3 Solvent Evaporation Losses

As explained in Section 3.3.2, we use here an adjustment factor of 1.0.

4.2.4.3.4 Petroleum Product Storage and Evaporation Losses

As shown in Section 3.3.3, it is reasonable to assume for this type of emission the same sensitivity to temperature as for vehicle evaporative emissions. We, therefore, assign a value of 1.16.

4.2.4.3.5 Gasoline Station Evaporation Losses

In accord with Section 3.3.3, we assign a sensitivity of 1.2 percent per degree, which leads to a factor equal to exp(0.012 x 8), or 1.10.

4.2.4.3.6 Chemical Manufacturing

In accord with Section 3.3.5, we assign a temperature adjustment factor of 1.0. (This category includes solvent losses from other industries besides manufacture of chemicals.)

4.2.4.3.7 Remaining Sources

In accord with Section 3.3.6, all remaining sources receive a temperature adjustment factor of 1.0.

4.2.4.4 Summary of Correction Factors

Table 4-3 presents a compilation of the correction factors for Tampa Bay, as discussed in preceding sections.

4.2.5 FINAL COMPUTATIONS AND TABULATIONS

Table 4-4 shows the results of this procedure for the Tampa Bay study area. Also shown, for ready comparison, are the annual emissions of reactive organics, computed by combining the annual emissions given in Table 4-2 with the methane correction factors given in Table 4-3.

The comparison shows that the net effects of seasonal corrections, for this study area, are rather small; total emission rates in summer are larger than the annual rates, but only by 2,400 MT/yr out of 72,400, approximately 3 percent. Exhaust emissions are about 4 percent lower in the summer, but automotive evaporation is increased by about 14 percent, so that the net increase in gasoline-powered vehicle emissions is 1,000 MT/yr, or about 2 percent. The order of importance of the various source categories is unaffected by the seasonal corrections.

Table 4-3. CORRECTION FACTORS FOR TAMPA BAY

Source Category	Correction Factors			
	Methane	Activity	Temp.	Overall
1. Gasoline-powered vehicles				
a. Exhaust emissions (65%)	0.95	0.98	0.98	0.91
b. Evaporative emissions (35%)	1.00	.98	1.16	1.14
2. Solvent evaporative losses	1.00	1.00	1.00	1.00
3. Petroleum product evaporation				
a. Storage and transport	1.00	1.00	1.00	1.00
b. Gasoline station losses	1.00	.98	1.10	1.08
4. Petroleum refineries	N/A	N/A	N/A	N/A
5. Solid waste disposal	.66	1.00	1.00	.66
6. Manufacturing	1.00	1.00	1.00	1.00
7. Stationary fuel combustion	.85	1.00	1.00	.85
8. Carbon black production	.62	1.00	1.00	.62
9. Aircraft	.93	1.00	1.00	.93
10. Diesel-powered vehicles	.94	.98	1.00	.92
11. Vessels	.91	1.00	1.00	.91

Table 4-4. REACTIVE ORGANIC EMISSIONS, TAMPA BAY

Source Category	Emissions			
	Summer		Annual	
	MT/yr	%	MT/yr	%
1. Gasoline-powered vehicles	42,400	(61)	41,400	(61)
a. Exhaust emissions	25,400	37	26,500	39
b. Evaporative emissions	17,000	24	14,900	22
2. Solvent evaporative losses	8,800	13	8,800	14
3. Petroleum product evaporation				
a. Storage and transport	7,100	1	6,100	1
b. Gasoline station losses	5,800	9	5,400	8
4. Petroleum refineries	0	0	0	0
5. Solid waste disposal	500	1	500	1
6. Manufacturing	2,700	4	2,700	4
7. Stationary fuel combustion	700	1	700	1
8. Carbon black production	0	0	0	0
9. Aircraft	800	1	800	1
10. Diesel-powered vehicles	1,400	2	1,400	2
11. Vessels	3,000	5	3,000	5
Remainder unlisted	1,600	2	1,600	2
Total	74,800	100	72,400	100

4.3 ST. LOUIS STUDY AREA

4.3.1 ANNUAL ORGANIC EMISSIONS

Emissions data for the St. Louis area were obtained from NEDS Emissions Reports for seven counties and the City of St. Louis. Totals by source category are shown in Table 4-5, the total for all categories coming to nearly 300,000 MT/yr. Emission rates for reactive organics, also shown in Table 4-5, were calculated by multiplying the total organic emissions entries by the corresponding methane correction factors shown in Table 4-3; the difference in totals indicates that methane emissions amounted to about 4,000 MT/yr.

Some of the categories listed in table 4-5 are slightly different from those given for Tampa Bay in Table 4-1. The changes were made to make the category list cover all the emissions in the NEDS list; thus, we refer to "petroleum industry" rather than "petroleum refineries" and to "other industries" instead of "manufacturing." This allows miscellaneous small items shown in Table 4-1 as "Remainder Unlisted" to be absorbed in the new categories.

The category, gasoline-powered vehicles, has been partitioned into subcategories a and b according to the same logic discussed in Section 4.2.2.

4.3.2 SUMMER ACTIVITY FACTORS

Vehicle activity factors were estimated from monthly reports of gasoline sales volume provided by the State of Missouri Department of Revenue. These reports dealt with sales throughout the entire State of Missouri; it is assumed that they provide a reasonable estimate of seasonal traffic variation in the study area. The factor thus derived was 1.04. It was applied to category 3b, gasoline station evaporation losses, and category 10, diesel-powered vehicles, as well as to exhaust emissions and evaporative emissions from gasoline-powered vehicles.

Table 4-5. ORGANIC EMISSIONS, ST. LOUIS STUDY AREA

Source Category	Emission Rates, MT/yr		%[a]
	Total	Reactive	
1. Gasoline-powered vehicles	121,700	(120,100)	(41)
a. Exhaust emissions (65%)	(79,100)	77,500	26
b. Evaporative emissions (35%)	(42,600)	42,600	15
2. Solvent evaporative losses	78,500	78,500	27
3. Petroleum product evaporation			
a. Storage and transport	33,600	33,600	11
b. Gasoline station losses	11,300	11,300	4
4. Petroleum industry	11,400	11,400	4
5. Solid waste disposal	4,000	2,700	1
6. Other industries	23,200	23,200	8
7. Stationary fuel combustion	2,800	2,400	1
8. Carbon black production	0	0	
9. Aircraft	2,800	2,600	1
10. Diesel-powered vehicles	4,200	3,900	1
11. Vessels	3,100	2,800	1
Total	296,700	292,600	100

[a] Percent of total reactive emissions

Because the specific NEDS point source reports which were examined (Section 3.2) indicated no consistent increase or decrease (in summer) of throughput or production in solvent-using or petroleum-related industry, we have chosen to use activity factors of 1.0 for all emission categories except those related to vehicle use. We note, however, that fluctuations of 5 to 10 percent in manufacturing employment, generally, are not uncommon within a given year. Some of this fluctuation may have a seasonal basis; in particular, manufacturing tends to decline in winter in cold climates.

4.3.3 TEMPERATURE ADJUSTMENT FACTORS

Climatological data for the St. Louis area show that the average daily maximum temperature for the summer quarter, t_s, is 86°F, while the average for the entire, t_a, is 66°F; thus $t_s - t_a$ is 20°F.

Using Table 3-1 and proceeding as explained in Section 4.2.4.3.1, we find the correction term for vehicle exhaust emissions for these temperatures to be 0.94.

The factor for evaporative emissions for gasoline-powered vehicles and for petroleum product storage and evaporation losses is calculated by equation 1, Section 3.3.1, as F_c (86,66) = exp (0.02 x 20) = 1.49. Similarly, the factor for gasoline station evaporation losses is exp (0.012 x 20) or 1.27, and that for petroleum industry is exp (0.005 x 20), or 1.10.

All other sources are assigned a temperature adjustment factor of 1.0.

4.3.4 FINAL COMPUTATIONS AND TABULATION

Table 4-6 summarizes the factors for activity and temperature corrections and lists the estimated reactive organic emission rates

for summer. These are obtained by multiplying the annual reactive emission rates shown in Table 4-5 by both factors.

Comparison of results in Tables 4-5 and 4-6 shows that the total rate of emissions in summer is about 41,000 MT/yr greater than the annual rate of 293,000 MT/yr. A large share of the increase is attributable to the increased estimate of petroleum product storage and transport losses, which increases from 33,600 to 50,100 MT/yr. Evaporative emissions from automobiles also increase by 23,000 MT/yr; this figure is sensitive not only to the factor taken for temperature adjustment but also to the percentage assumed to be evaporative, in partitioning the total emissions from the gasoline-powered vehicles.

4.4 BUFFALO STUDY AREA

4.4.1 ANNUAL ORGANIC EMISSIONS

Emissions data from the Buffalo area were obtained from a NEDS Emission Report for the Niagara Air Quality Control Region, comprising the counties of Niagara and Erie, in New York. Totals by source category are shown in Table 4-7; the total for all categories, including methane, is about 120,000 MT/yr. Emission rates for reactive organics, also shown in Table 4-7, were calculated by multiplying the total organic emissions entries by methane correction factors from Table 4-3. The total methane correction is 2,900 MT/yr, slightly more than 2 percent of the total.

Categories listed in Table 4-7 are the same as those listed in Table 4-5; for discussion, refer to Section 4.3.1.

4.4.2 SUMMER ACTIVITY FACTORS

Vehicle activity factors were estimated from monthly reports of gasoline sales volume for Erie and Niagara Counties, provided by the Energy Office of the State of New York. These reports

Table 4-6. EMISSIONS OF REACTIVE ORGANICS, SUMMER, ST. LOUIS

Source Category	Factors		Emissions (Summer)	
	Activity	Temp.	MT/yr	%
1. Gasoline-powered vehicles			(139,000)	(42)
a. Exhaust emissions	1.04	0.94	73,500	22
b. Evaporative emissions	1.04	1.49	66,000	20
2. Solvent evaporation losses	1.00	1.00	78,500	24
3. Petroleum product evaporation				
a. Storage and transport	1.00	1.49	50,100	15
b. Gasoline station losses	1.04	1.27	14,900	4
4. Petroleum refineries	1.00	1.10	12,500	4
5. Solid waste disposal	1.00	1.00	2,700	1
6. Manufacturing	1.00	1.00	23,200	7
7. Stationary fuel combustion	1.00	1.00	2,400	1
8. Carbon black production	N/A	N/A	0	1
9. Aircraft	1.00	1.00	2,600	1
10. Diesel-powered vehicles	1.04	1.00	4,100	1
11. Vessels	1.00	1.00	2,800	1
Total			333,300	100

Table 4-7. ORGANIC EMISSIONS, BUFFALO STUDY AREA

Source Category	Emission Rates, MT/yr		%[a]
	Total	Reactive	
1. Gasoline-powered vehicles	50,900	(49,200)	(42)
a. Exhaust emissions (65%)	(33,100)	31,400	26
b. Evaporative emissions (35%)	(17,800)	17,800	15
2. Solvent evaporative losses	49,100	49,100	42
3. Petroleum product evaporation			
a. Storage and transport	0	0	
b. Gasoline station losses	4,500	4,500	4
4. Petroleum industry	1,600	1,600	1
5. Solid waste disposal	2,300	1,500	1
6. Other industries	7,600	7,600	6
7. Stationary fuel combustion	1,300	1,100	1
8. Carbon black production	N/A	N/A	N/A
9. Aircraft	1,200	1,100	1
10. Diesel-powered vehicles	800	800	1
11. Vessels	900	800	1
Total	120,200	117,300	100[b]

[a] Percent of total reactive emissions

[b] Slight discrepancies in the total may be caused by rounding

indicated that the rate of gasoline consumption in summer was about 1.02 times the annual rate. This factor was applied to categories 1a, 1b, 3b, and 10, all related to vehicle activity. Other categories were assigned activity factors of 1.0, following the reasoning set forth in Section 4.3.2.

4.4.3 TEMPERATURE ADJUSTMENT FACTORS

Climatological data for the Buffalo area show that the average daily maximum temperature for the summer quarted is 77°F while the year-round average is 56°F, an increment of 21°F. Using Table 3-1, the correction factor for vehicle exhaust emissions is found to be 0.93. This is smaller than the corresponding factor for St. Louis (0.94; refer to Section 4.3.3) not only because of the slightly larger temperature increment in Buffalo (21° versus 20°F) but also because of the lower overall temperature, 56° versus 66°F).

The factor for evaporative emissions of gasoline-powered vehicles and for petroleum product storage and evaporation losses is 1.52; for gasoline station evaporation losses, 1.29; and for petroleum industry, 1.10. (Calculations are analogous to those explained in Section 4.3.3.)

All other sources are assigned a temperature adjustment factor of 1.0.

4.4.4 FINAL COMPUTATIONS AND TABULATION

Table 4.8 summarizes the factors for activity and temperature corrections and lists the estimated reactive organic emission rates for summer. These are obtained by multiplying the annual reactive organic emission rates shown in Table 4-7 by both factors.

Comparison of Tables 4-7 and 4-8 shows an increase in total reactive organic emissions in the summer of about 10,000 MT/yr.

Table 4-8. EMISSIONS OF REACTIVE ORGANICS, SUMMER, BUFFALO

Source Category	Factors		Emissions (Summer)	
	Activity	Temp.	MT/yr	%
1. Gasoline-powered vehicles			(57,400)	(45)
a. Exhaust emissions	1.02	0.93	29,800	23
b. Evaporative emissions	1.02	1.52	27,600	22
2. Solvent evaporation losses	1.00	1.00	49,100	39
3. Petroleum product evaporation				
a. Storage and transport	1.00	1.52	0	0
b. Gasoline station losses	1.02	1.29	5,900	5
4. Petroleum refineries	1.00	1.10	1,800	1
5. Solid waste disposal	1.00	1.00	1,500	1
6. Manufacturing	1.00	1.00	7,600	6
7. Stationary fuel combustion	1.00	1.00	1,100	1
8. Carbon black production	N/A	N/A	N/A	
9. Aircraft	1.00	1.00	1,100	1
10. Diesel-powered vehicles	1.02	1.00	800	1
11. Vessels	1.00	1.00	800	1
Total			127,100	100[a]

[a] Slight discrepancies in the total may be due to rounding.

This is only a 9 percent increase, compared to 14 percent for St. Louis, and is largely due to evaporative emissions from gasoline vehicles. It should be pointed out, however that in NEDS there are no reported emisions for petroleum product storage and transport in the Buffalo area. This category accounted for 11 percent of annual emissions and 15 percent of estimated summer emissions for St. Louis.

5.0 DISCUSSION AND CONCLUSIONS

The results described in Section 4.0 show that the effect of summer conditions can be either an increase or a decrease in emissions relative to the annual average, depending on the particular circumstances of the region involved. It is clear, also, that the results for a given region depend on what values are assumed for various parameters required in the computations, and on other assumptions having uncertain validity. Some of these assumptions are reviewed in this section.

5.1 PARTITION OF VEHICULAR EMISSIONS

The differences in temperature sensitivity of various modes of emission of organics from light-duty gasoline-powered vehicles were described in Section 3.3.1. Since the emission factors for the various modes are all composites, based on different values for many different model-years and makes, the values of these emission factors must be continually changing as the composition of the vehicle population changes. Vehicle air conditioner usage also may have a significant effect in some areas.

Vehicle air conditioner usage was not known but would probably have negligible effect on Tampa Bay emissions. If our rough estimate of an air conditioner usage factor of 1.07 were applied to St. Louis exhaust emissions, it would increase the calculated total reactive organic emissions in that city by 5,100 metric tons per year, or less than 2 percent.

It appears that the uncertainty as to the correct partition of vehicle emissions will contribute some uncertainty in the determination of temperature corrections in any urban area subject to photochemical oxidant air pollution.

5.2 TEMPERATURE VARIATION IN STORED LIQUIDS

As explained in Section 3.3, we have assumed that temperature effects on storage and transport of petroleum products amount to about 2 percent per degree (Fahrenheit), which is the same as the temperature sensitivity of vapor pressure of petroleum products. Nevertheless, some storage tanks may exhibit much higher temperature sensitivity (up to 7 percent per degree, at least), while others may have less, because of different systems of vapor control. Again, volatility is a function not of ambient temperature, but of the temperature of the stored liquid. We know of no information on the actual seasonal variation in tank temperatures through the year, but they may be expected to be at least somewhat less than variations in ambient temperature. The assumed sensitivity (2 percent per degree) may be reflected in errors in the estimated emissions.

Thus, for St. Louis, a sensitivity of 3 percent per degree would increase the summer emissions estimate by another 10,000 MT/yr, or 3 percent of the total reactive organic emissions.

5.3 EFFECT OF ECONOMIC CONDITIONS

Activity factors are based on the concept that emissions vary cyclically through the year in response to cyclic variations of the activities that produce them. The cyclic hypothesis, however, is an imperfect one in every instance; activity factors based on it will be found to vary from year-to-year, as the rate of such activities is confounded with short-term fluctuations and long-term trends which have no detectable seasonal basis. If a gasoline shortage should occur during the summer in an area with much summer tourist travel, a substantial distortion of normal seasonal traffic emissions might be encountered. Other economic disturbances can cause reduced employment and reduced emissions in manufacturing

industries. Thus, even an established seasonal pattern is not necessarily a reliable tool for prediction of the seasonal effect in any given year.

5.4 INTERPRETATION OF NEDS CATEGORIES

A problem which can introduce uncertainty into the estimation of summer emissions arises from the fact that not all suppliers of information to the NEDS data base have been completely consistent in their assignment of particular source emissions to the available emissions categories. In the case of the Buffalo study area, no emissions were reported in the category of losses from storage and transport of petroleum compounds, although it seems hardly credible that there should be no such facilities in an urban area as well populated as the "Niagara Frontier." On the other hand, some 8,000 tons per year have been listed under "Other/not classified;" if these were assumed to be storage and transport losses, the summer emissions total for Buffalo would be increased by another 4,000 tons or about 3 percent of the organic emissions total. In the particular case of Buffalo, this would raise the summer emissions from 100 percent to 103 percent of the annual emissions.

Again, for Tampa Bay, the NEDS summaries reported no "gasoline sta evap loss" under miscellaneous area sources, a category which accounted for 11,000 MT/yr in St. Louis. In the Tampa Bay emissions survey, PES identified losses from gasoline service stations in Tampa Bay, arriving at a total of 5,400 MT/yr. The NEDS summaries do carry, however, under transportation area sources, an item of nearly 6,000 MT/yr titled "gas handling evaporation loss," which does not appear in the summaries for St. Louis and Buffalo.

Thus, care is needed in the interpretation and transcription of the data presented in the NEDS summaries.

5.5 CONCLUSIONS

The findings set forth in Section 4.0 show that emission rates of reactive organics in urban areas in summer could be either greater or less than the year-round average emission rates. In general, emissions from gasoline-powered vehicle exhausts decrease with increasing temperature, while evaporative emissions from vehicles, evaporation of petroleum products (in storage, transport, and marketing), and perhaps petroleum refinery operations increase with increasing temperature. The balance of these effects determines whether the net effect in summer will be an increase or a decrease.

On the whole, it may be expected that, in areas like Tampa Bay, where motor vehicles generate a relatively large share of the organic emissions, emissions will be very near the annual average in summer. In more highly industrial locations such as St. Louis, emissions are likely to be higher than average in summer.

Methane emissions in the areas studied were estimated to be about 2 percent of the total organic emissions.

Corrections for seasonal variations in activities which cause organic emissions did not cause any significant alterations in the order of relative importance of various emissions source categories. In all the study areas investigated, at least 80 percent of the reactive organic emissions were generated by three categories: gasoline-powered vehicles, solvent evaporation from area sources, and evaporation of petroleum products.

A methodology for estimating summer emission rates of reactive organics has been outlined, and formulas and tables have been presented for computing temperature corrections for emissions from various source categories.

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